

DESULFURIZATION OF ORGANIC COMPOUNDS AND COAL-DERIVED LIQUIDS BY NOVEL TRANSITION METAL COMPLEXES

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Introduction

In producing environmentally acceptable fuels by coal liquefaction, the removal of organic sulfur- and nitrogen-containing components from such coal-derived liquids poses a serious problem. Existing desulfurization and denitrogenation methods generally require elevated temperatures, high pressures of hydrogen and the use of heterogeneous catalysts. If efficient methods for heteroatom removal could be found, which are operative at lower temperatures and pressures, then a significant saving in process equipment and energy might be realized in preparing clean fuels from coal.

In order to design such improved desulfurization and denitrogenation methods for coal-derived liquids, it is important to learn about the experimental factors that foster the cleavage of carbon-sulfur and carbon-nitrogen bonds under mild conditions (1). We have sought reagents or catalysts that can cleave such bonds at atmospheric pressure, in the temperature range of 25-125°C and in homogeneous media. The reagents chosen have been metal complexes of nickel, cobalt, iron and molybdenum, which are miscible in organic solvents, such as tetrahydrofuran and toluene. As a reducing agent or hydrogen source, we have employed the transition metal complex itself, in a subvalent state, or a metal hydride, such as LiAlH_4 , R_2AlH or $\text{NaAlEt}_2\text{H}_2$.

Before applying such reagents to coal-derived liquids, we have evaluated their desulfurizing or denitrogenating action on a variety of model compounds, whose structures are similar to those of organosulfur or organonitrogen components found in coal liquefaction products. The principal model sulfur compounds under study have been dibenzothiophene (1), phenothiazine (2), phenoxathiin (3), thianthrene (4), aryl mercaptans (5), dibenzyl sulfide (6) and dibenzyl disulfide (7). In our denitrogenation studies, which are in a very early stage, we have chosen carbazole (8), indole (9) and quinoline (10) derivatives as model nitrogen compounds.

In the present article we wish to discuss, in detail, our findings on how efficiently nickel(0) or cobalt(I) complexes can desulfurize dibenzothiophene in tetrahydrofuran solution at 55°C. This study has provided insight into the factors favoring the cleavage of carbon-sulfur bonds. Our understanding of the reaction mechanism for desulfurization should prove helpful in designing more active and efficient desulfurizing agents for coal liquids (2).

EXPERIMENTAL

Starting Materials

The organic sulfur compounds were obtained commercially in a good grade of purity or were synthesized by known procedures and were recrystallized or purified by column chromatography, until their melting points and spectra accorded with literature values. Bis (1,5-cyclooctadiene) nickel(0) and 1,5-cyclooctadiene (3-cyclooctenyl) cobalt(I) were prepared by modifications of reported methods (3,4); commercial 2,2'-bipyridyl was recrystallized from ethyl acetate to constant m.p. of 71-73°C; tetrahydrofuran and toluene were purified by heating at reflux over sodium-potassium alloy in the presence of some benzophenone.

General Techniques

All manipulations involved in the preparation, storage and transfer of organonickel complexes and their reaction products were conducted under an atmosphere

of dry and oxygen-free argon. The chromatographic and spectral instrumentation used in the separation and identification of the reaction products has been described elsewhere (5).

Typical Reaction Procedure

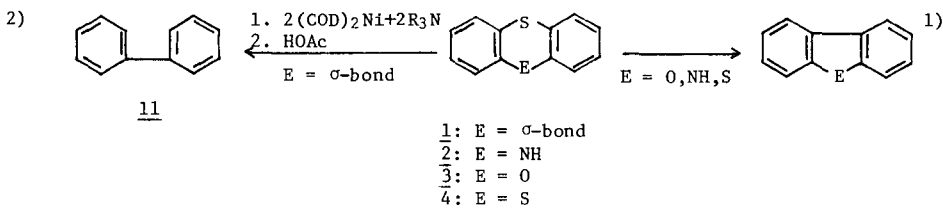
A pale yellow solution of 3.3 mmol of bis (1,5-cyclooctadiene) nickel(0) in 15 ml of THF under an argon atmosphere was treated with 3.3 mmol of 2,2'-bipyridyl in 5 ml of THF, whereupon the solution turned the violet-blue color of the 2,2'-bipyridyl (1,5-cyclooctadiene) nickel(0) complex. The solution was then treated with 1.6 mmol of the sulfur compound and the temperature maintained between 40°C and 70°C for 24 to 48 h. The reaction mixture was worked up in one of two ways: either glacial acetic acid was added and the mixture stirred; or powdered LiAlH_4 was added and the mixture allowed to stir for a time. In either case, cautious addition of water and ethyl ether was followed by separating the organic layer, neutralizing it, if necessary, with aqueous NaHCO_3 solution and drying over anhydrous Na_2SO_4 . Removal of the solvent gave a residue that was analyzed by chromatographic and spectral means.

In those reactions where a combination of the Ni(0) or Co(I) complex and LiAlH_4 was used for desulfurization, these components were allowed to interact with each other for 30 min. before the organosulfur compound was added.

RESULTS

Desulfurization

Treatment of sulfur heterocycles 2-4 with two equivalents of a 1:1 mixture of bis (1,5-cyclooctadiene) nickel(0) [$(\text{COD})_2\text{Ni}$] and 2,2'-bipyridyl [bipy] gives, upon work-up with acid or LiAlH_4 , preponderantly, the desulfurized, ring-contracted heterocycles 50-70%, Equation 1). In contrast, dibenzothiophene (1) produced biphenyl (11) in 50% yield by work-up with glacial acetic acid but in 90% yield by work-up with LiAlH_4 (Equation 2):



1. **Amine Activation.** The contact of $(\text{COD})_2\text{Ni}$ alone with dibenzothiophene in warm THF causes little or no desulfurization. The action of two equivalents each of $(\text{COD})_2\text{Ni}$ and an amine brings about maximum desulfurization, under the conditions and work-up procedure given in Equation 2. The influence of the amine R_3N , on the extent of desulfurization is presented in Table I. It is noteworthy that bipyridyl (12) is the most effective amine, significantly superior to phenanthroline (13). Since phenanthroline has a rigidly planar structure, entropy factors should be less than with 12. Possibly, however, the increased back-bonding from nickel complexed with 13 causes the nickel-phenanthroline complex to transfer electrons to the organosulfur substrate less readily. In addition, the greater basicity of the amine is important (cf. 4-dimethylaminopyridine and pyridine), as is steric hindrance at the nitrogen (cf. ethylenediamine and tetramethylethylenediamine).

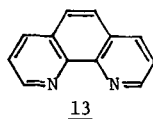
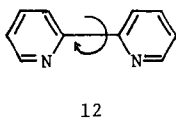


TABLE I

Desulfurization of Dibenzothiophene by (COD)₂Ni and an Amine

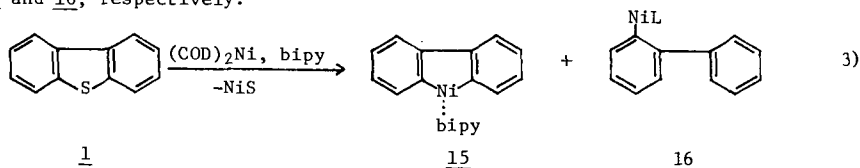
<u>Amine</u>	<u>Yield of Biphenyl (%)</u>
2,2'-Bipyridyl	45
4-Dimethylaminopyridine	21
Ethylenediamine	17
1,10-Phenanthroline	16
Pyridine	14
Hexamethylphosphorus triamide	14
N,N,N',N'-Tetramethylethylenediamine	8
1,8-Bis-dimethylaminonaphthalene	7
N,N'-Dimethylpiperazine	4
No amine added	< 1

Conditions: 55°C for 48 h with 2 equiv. of (COD)₂Ni,
work-up of HOAc

2. Coordination at the Nickel Atom. When one equivalent of dibenzothiophene is heated with one equivalent each of (COD)₂Ni and bipyridyl under the conditions given above, only 11% of biphenyl is formed. Moreover, when a 1:2:2 mixture of dibenzothiophene, (COD)₂Ni and bipyridyl (*cf. supra*) is augmented by one or more additional equivalents of bipyridyl, the conversion to biphenyl falls from 45% (Table I) to under 10%. Thus, two equivalents of the nickel(0) complex whose metal centers have available coordination sites, seem best-suited for a facile reaction with dibenzothiophene.

It is known that (COD)₂Ni and bipyridyl react to form (COD)Ni(bipy) (14) (6). From the above results, then, it is suggested that 14 complexes with 1 to yield (1) Ni(bipy); any additional 12 could compete with 1 for 14.

3. Intermediates in Desulfurization. The rupture of the carbon-sulfur bond can be represented as an oxidative addition by nickel(0), whereby nickel(II), both as NiS and as 15, is formed. Evidence for these products is the following: a) nickel(II) sulfide manifests itself as a black precipitate as the reaction proceeds; this precipitate dissolves in glacial acetic acid or rather concentrated aqueous HCl to evolve H₂S; and b) evidence for organonickel intermediates, such as 15, comes from work-up of the reaction with O-deuterioacetic acid; the resulting biphenyl contained 42% of 2,2'-dideuteriobiphenyl, 28% of 2-deuteriobiphenyl and 29% of undeuterated biphenyl (equation 3). The deuterated biphenyls point to the presence of 15 and 16, respectively.



Thus, about half the biphenyl's ortho positions were bonded to nickel prior to protolysis; prior to work-up, the other half had acquired protons, presumably from the solvent, tetrahydrofuran.

4. Effect of Substituents on the Ease of Desulfurization. To learn the effect of substituents, we first attempted to conduct competition experiments between dibenzothiophene and individual substituted derivatives. However, complexation of the nickel caused mutual retardation of desulfurization and low conversion even for dibenzothiophene itself. Consequently, we had to resort to a comparison of the

extents of desulfurization for individual compounds under our standard conditions (2 equiv. of $(\text{COD})_2\text{Ni}$ in THF for 48h at 55°C). The results are given in Table II. From these data we can conclude that methyl groups markedly retard the desulfurization: the retardation is greatest with methyl groups at the 3- and 7-positions, and one methyl group at the 2-position is about as retarding as methyl groups at both the 2- and 8-positions.

When these desulfurization reactions were worked up with O-deuterioacetic acid, the resulting biaryls were significantly less deuterated when methyl groups were attached to the ring. Thus, work-up of the 2,8-dimethyldibenzothiophene reaction gave 3,3'-bitolyl that was 7.8% dideuterated, 1.3% mono deuterated and 90.9% undeuterated. Similar work-up of 2-methyldibenzothiophene gave 3-methylbiphenyl that was 2.9% dideuterated, 23.8% monodeuterated and 73.3% undeuterated.

TABLE II

Desulfurization of Dibenzothiophenes by $(\text{COD})_2\text{Ni}$ and Bipyridyl

<u>Compound</u>	<u>Yield of Substituted Biphenyl (%)</u>
Parent DBT (1)	45
2,8-Dimethyl DBT	12
2-Methyl DBT	12
3,7-Dimethyl DBT	< 5

The decreasing ease with which methylated dibenzothiophenes undergo desulfurization is consistent with the importance of electron transfer.

Hydrodesulfurization

An even more potent desulfurizing agent resulted from combining $(\text{COD})_2\text{Ni}$, bipyridyl and LiAlH_4 . All the sulfur heterocycles 1-4 were converted by this combination into open-chain products, namely biphenyl, diphenylamine, diphenyl ether and benzene respectively (cf. Equation 1).

1. Amine Activation. Dibenzothiophene in tetrahydrofuran was treated at 55°C for 48 h with two equivalents each of $(\text{COD})_2\text{Ni}$, LiAlH_4 and the amine. The yields of biphenyl obtained after protolytic work-up are listed in Table III. From these results it is clear that the LiAlH_4 -containing reagent is a more powerful desulfurizing agent than the combination of $(\text{COD})_2\text{Ni}$ and an amine alone. With LiAlH_4 present, the activity of the reagent is not so sensitive to the nature of the amine. Although bipyridyl again activates most strongly, most of the amines show a comparably good activation.

TABLE III

Desulfurization of Dibenzothiophene by $(\text{COD})_2\text{Ni}$, LAH and an Amine

<u>Amine</u>	<u>Yield of Biphenyl (%)</u>
2,2'-Bipyridyl	93
Ethylenediamine	91
Hexamethylphosphorus triamide	86
N,N,N',N'-Tetramethylenethylenediamine	79
Pyridine	75
N,N'-Dimethylpiperazine	74
1,10-Phenanthroline	67
4-Dimethylaminopyridine	51

2. Labeling Studies. To learn something about the intermediates

involved in these desulfurizations, deuterium-labeled hydride and proton sources were used. When LiAlD_4 was employed and work-up involved ordinary acetic acid, the resulting biphenyl was 14% dideuterated, 25% monodeuterated and 60% undeuterated. When LiAlH_4 was used but the work-up employed O-deuterioacetic acid, the biphenyl obtained consisted of 94% undeuterated, 2% monodeuterated and 3% dideuterated product. Therefore, only about 4% of the biphenyl acquired its proton from CH_3COOD ; and about 22% of the biphenyl obtained its hydrogen from the LiAlH_4 . Accordingly, about 75% of the biphenyl obtained its hydrogen from the reaction-medium, presumably from the tetrahydrofuran.

3. Desulfurization with Nickel(II) Salts and Metal Hydrides. In attempts to generate in situ nickel(0) complexes suitable for desulfurization, two equivalents each of nickel(II) acetylacetonate and bipyridyl were treated with LiAlH_4 or $i\text{-Bu}_2\text{AlH}$. The conversions of dibenzothiophene to biphenyl ranged from 35-40%. Thus, a moderately active desulfurizing agent can be generated in situ.

4. Cobalt Complexes. The hydrocarbon-soluble complex, 1,5-cyclooctadiene (3-cyclooctenyl)cobalt (17), was synthesized and its action on dibenzothiophene studied (Table IV). From this, we conclude that $\text{COD}(\text{C}_8\text{H}_{13})\text{Co}$ with bipyridyl is not as effective as $(\text{COD})_2\text{Ni}$ with bipyridyl. On the other hand, $\text{COD}(\text{C}_8\text{H}_{13})\text{Co}$ combined with LiAlH_4 is as good as, even possibly better than, $(\text{COD})_2\text{Ni}$ with LiAlH_4 . Furthermore, with the cobalt complex, bipyridyl is not necessary and in fact retards the desulfurization.

TABLE IV

Desulfurization of Dibenzothiophene with $\text{COD}(\text{C}_8\text{H}_{13})\text{Co}$

<u>Reagent</u>	<u>Conditions</u>	<u>Yield of Biphenyl (%)</u>
$\text{COD}(\text{C}_8\text{H}_{13})\text{Co}$	1 equiv.	5
$\text{COD}(\text{C}_8\text{H}_{13})\text{Co}$	2 equiv.	10
$\text{COD}(\text{C}_8\text{H}_{13})\text{Co}$	1 equiv. + bipyridyl	10
$\text{COD}(\text{C}_8\text{H}_{13})\text{Co}$	2 equiv. + 2 equiv. of bipyridyl	18
$\text{COD}(\text{C}_8\text{H}_{13})\text{Co}$	1 equiv. + 1 equiv. each of bipyridyl and LiAlH_4	60
$\text{COD}(\text{C}_8\text{H}_{13})\text{Co}$	2 equiv. + 2 equiv. each of bipyridyl and LiAlH_4	87
$\text{COD}(\text{C}_8\text{H}_{13})\text{Co}$	2 equiv. + 2 equiv. LiAlH_4	97

5. Other Metals. Thus far, cyclopentadienyl derivatives of iron, titanium and molybdenum, when combined with LiAlH_4 , show little desulfurizing activity (~5%) toward dibenzothiophene. A combination of MoCl_5 and $i\text{-Bu}_2\text{AlH}$ in refluxing toluene did yield ~15-20% of biphenyl.

6. Coal-derived Liquids. Preliminary studies on desulfurizing Solvent-Refined-Coal liquids have shown that the $(\text{COD})\text{Ni}$ -bipyridyl- LiAlH_4 reagent in THF can reduce the organic sulfur content significantly (0.5%→0.3%). Reaction conditions have not yet been optimized.

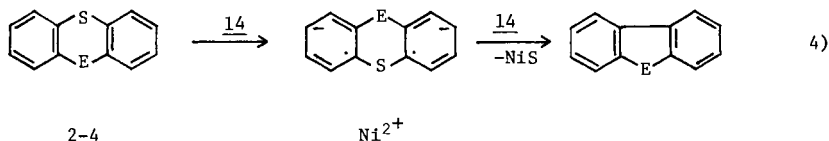
DISCUSSION

In any discussion of reaction mechanisms for desulfurizations by these nickel reagents, it is clear that different pathways must be proposed for the cyclizing desulfurization (Equation 1) and the hydrodesulfurization processes (Equation 2), respectively. In the latter reaction, the role of the lithium aluminum hydride cannot be assigned with any confidence until the stoichiometry of the separate reactions of the hydride with both $(\text{COD})_2\text{Ni}$ and with bipyridyl has been determined. A preliminary suggestion has been published that the hydride and $(\text{COD})_2\text{Ni}$ can form

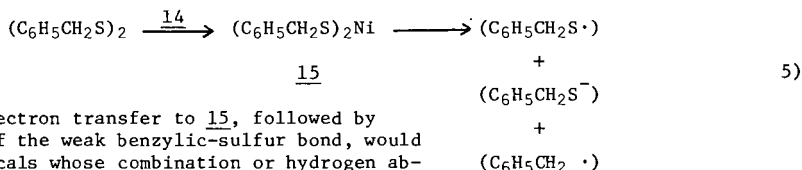
a complex of the type, $\text{Li}[\text{H}_3\text{AlNiAlH}_3]$, but supporting data are unavailable (7). For the present, therefore, attention will be devoted to the hydride-free nickel reagent, $(\text{COD})_2\text{Ni}$ and bipyridyl.

The striking color change when a yellow solution of $(\text{COD})_2\text{Ni}$ is treated with bipyridyl can be assigned to the formation of the deep blue-violet 2,2'-bipyridyl 1,5-cyclooctadiene) nickel(0) complex (14), as demonstrated by the proton magnetic resonance spectrum of the complex, which shows only one olefinic bond coordinated with the nickel (6). Complex 14, the active desulfurizing agent in the aforementioned processes, would appear to function in many of its reactions as an electron-transfer reagent. Several lines of evidence support such a mode of action for 14: 1) deoxygenation of certain epoxides to olefins occurs in a nonstereoselective manner (8); 2) dehalogenation of β,β,β -triphenylethyl bromide occurs, in part, with rearrangement to α,α,β -triphenylethyl radicals (9); and 3) the accelerating effect of donor solvents on the cleavage reactions of 14 is in accord with such electron transfer (8).

In the present desulfurization studies the ring contraction observed when phenoxathiin, phenothiazine or thianthrene is treated with $\text{bipy}(\text{COD})\text{Ni}$ (14) can be understood as an instance of such electron transfer (Equation 4):



The cleavage of open-chain sulfur compounds can also be viewed in terms of electron transfer: by either cleavage of the disulfide by nickel(0) or by reaction of the mercaptan with nickel(0), 15 can be formed (Equation 5):



Further electron transfer to 15, followed by cleavage of the weak benzylic-sulfur bond, would yield radicals whose combination or hydrogen abstraction from the medium could lead to the observed products, $\text{C}_6\text{H}_5\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$ and $\text{C}_6\text{H}_5\text{CH}_3$. In an analogous manner, dibenzyl sulfide would be expected to undergo facile cleavage to the radical, $\text{C}_6\text{H}_5\text{CH}_2\cdot$, via an electron-transfer-induced scission.

As mentioned at the start of this section, the ill-defined nature of the $(\text{COD})\text{Ni}$ -bipyridyl- LiAlH_4 agent makes any detailed mechanistic discussion of its action inappropriate at this time. However, certain characteristics of the LiAlH_4 -containing desulfurizing agent are worthy of comment. When LiAlD_4 is employed with 14 for desulfurizing dibenzothiophene, no deuterium is found in the biphenyl produced. These results clearly show that the hydrogen source in such a hydrodesulfurization is the medium. In light of other evidence on electron-transfer in related nickel systems, it is suggested that transitory aryl radicals rapidly abstract hydrogen from the tetrahydrofuran.

The unifying feature of these desulfurization and hydrodesulfurization processes, therefore, appears to be the operation of an electron-transfer mechanism. The low-valent nickel or cobalt center can be induced to transfer electrons

to the aromatic sulfur compound by increasing the metal atom's electron density by coordinating hydride, amine or ether donors to it. Such electron transfer then sets the stage for carbon-sulfur bond scission.

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